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IV.

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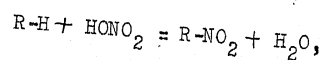
THEORY OF NITRATING SATURATED HYDROCARBONS AND THEIR
DERIVATIVES

IV ON THE MECHANISM OF OXIDATION OF THE PARAFFIN CHAIN
BY NITRIC ^{OGEN} OXIDES AND NITRIC ACID

A. I. Titov

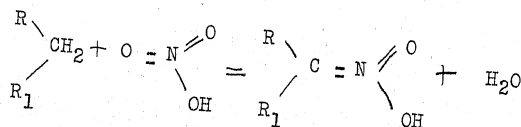
Formation of oxidation products appears to be one of the basic and frequently even the main reaction in the nitrating of saturated hydrocarbons. The problem of how oxidation products are formed ^{has} received special attention from those experts on nitrating the paraffin chain, M. I. Konovalov and S. S. Nametkin.

Konovalov(1), proceeding from the usual ideas about the mechanism of nitrating as a double decomposition reaction:



thought that nitro compounds ~~were~~ ^{were} the sole and the primary products of nitrating. He assumed that the products of oxidation -- aldehydes, ketones, and acids -- are formed in this reaction through a ^{subsequent} ~~Allegible~~ conversion of nitro derivatives. When experiment showed the ^{stability} ~~Allegible~~ persistence of nitro-substitutions in the paraffin chain, under conditions of nitrating, Konovalov, ^{substituted} ~~substituted~~ tried to ^{retain} ~~preserve~~ the reaction mechanism he ^{postulated} ~~accepted~~. Accordingly he introduced a hypothesis about the initial formation of nitro compounds in unstable, chemically active forms whose conversions led, in his opinion, to the formation of oxidation products.

S. S. Nametkin (2), arrived at a somewhat similar conclusion. According to his ideas about the mechanism of nitrating paraffins, initial products of the reaction ₂ (for obtaining primary and secondary nitro compounds) are acid salts:

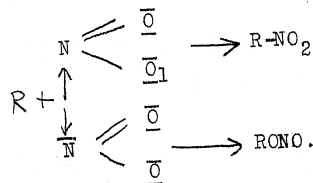


He used the Nef conversion of isonitro compounds into aldehydes and ketones to account for the formation of the latter and, subsequently, for the formation of carboxylic acids as well.

Unfortunately, in the purely theoretical researches of other investigators, this very important aspect of the reaction (in the nitrating of the paraffin chain and of alkyl benzenes) was completely ignored. The theory of nitrating the paraffin chain, developed by us (3), led to the correct explanation for the formation of oxidation-products, and also to several fundamental discoveries in this field.

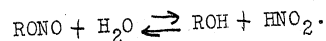
According to our theory, the primary reaction of nitrating the paraffin chain is the reaction between the hydrocarbon and nitrogen dioxide monomer yielding free radicals:

As shown in communication 2 II, ~~the most probable transformation of alkyls in the sphere of nitration would be combination with nitrogen oxide and dioxide. Taking into consideration the resonance structure of the nitrogen dioxide monomer, it is to be expected that its reaction with the alkyl will go in two directions:~~

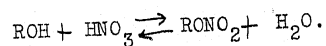


Since NO_2 has a primary structure with an unpaired electron ^{at N}, a nitro compound should be formed with the nitrogen, but due to a preponderance of the secondary form with a free valence ^{at N}, there should also be formed alkyl nitrite having one or the other atoms of oxygen. This conclusion is the starting point in developing our theory of oxidation-product formation and destruction during nitration of the paraffin chain.

The alkyl nitrites so formed during the nitrating ^{or} should, in the liquid phase, ^{shown} rapidly undergo a series of reactions. For instance, in ^{an} acid medium, they will be very easily hydrolyzed:



The resulting alcohol reacts with nitric acid - always present in the nitrating medium - to form alkyl nitrate:

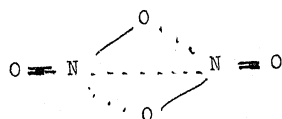


As a result of the above reactions including ^{or} esterification and other possible processes involving nitric ^{or} oxides, an equilibrium should

speedily be established, at least between the three compounds: alkyl nitrite, alcohol, an alkyl nitrate. Along with these one can also expect formation of ethers and esters of carboxylic acids evolved upon further oxidation of alcohol.

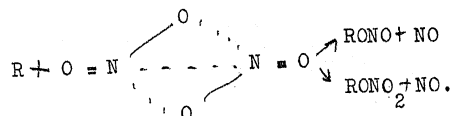
Besides this basic technique of forming alcohols and their esters, we could show other possible ways of doing so which under given conditions might be of great importance.

Let us examine from this point of view the reaction of alkyls with nitrogen dioxide dimer, N_2O_4 . If we make use of ^{the} ideas about the construction of nitrogen oxides, which we had developed (3), then the usual structural formula of ~~N_2O_4~~ ^{N_2O_4} may be refined into:

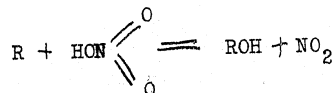


in which the ^{indicate} dots ~~chemical~~ bonds of a secondary order: $(\text{O} \cdots \text{N})$, for an electrostatic and $(\text{N} \cdots \text{N})$, for a resonant type.

Since the nitrogen atoms are shielded in this structure, the reaction of alkyls with ~~N_2O_4~~ ^{N_2O_4} should yield nitrous and nitric esters:

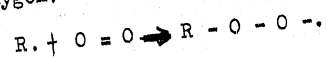


As the collision efficiency of radicals with N_2O_4 will be many times less than it would be for NO and NO_2 , the above shown reaction should be significant only at low concentrations of nitrogen oxide and of nitrogen dioxide monomer. From spatial and energy computations, we assume that very rare collisions of radicals with the molecule of nitric acid will form some alcohols.



The significance of this process appears only at sufficiently high temperatures, in high concentrations of nitric acid but low concentrations of nitric oxides. The last conclusion also applies to the improbable re-

action of alkyls with oxygen:



which may, all things considered, form alkyl nitrates by a further reaction with nitrogen oxide, for example.

Finally, it must be said, the effective collision of radicals with N_2O_3 , ~~as can be concluded from a number of data,~~ according to a series of ~~illegible-illegible-illegible-illegible~~ leads only partially to the formation of alkyl nitrite and to a greater degree to the formation of nitroso and nitro compounds (4).

In summing up this theoretical investigation, it appears definite that alkyl nitrite, alcohol, and alkyl nitrate, are among the products formed during the nitrating of the paraffin chain. The formation of these compounds has been unsuspected until now. Nevertheless, by creating favorable conditions for the retention of the alcohols, and their nitrous and nitric esters, we succeeded in directing the reaction toward their formation in significant quantities in complete agreement with theory.

The sought-for alcohol, nitrite, and nitrate were found in the residue from nitrating alkyl benzenes in the paraffin chain, after the removal of nitro compounds and acids. This will be referred to from now on as residual oil. This problem had been studied in the greatest detail following similar investigations on the nitrating of toluene. Guided by theory, we succeeded in proving in this case that the yield of residual oil, of desirable composition, was up to 40 and more percent of the entire product of the reaction. Particularly important for the preservation of the desired products was the employment of a large excess of hydrocarbon. By utilizing conclusions about reactions of radicals with N_2O_4 , by employing excess hydrocarbon and dehydrating agents, and by oxidizing nitrogen oxide out of the sphere of reaction, we so directed the reaction between toluene and nitrogen dioxide at usual temperatures as to obtain a preponderance of benzyl nitrate.

Discovery of the formation of alkyl nitrites, alcohols, and alkyl nitrates during the nitrating of the paraffin chain made clear the natural process of obtaining the oxidation products: aldehydes, ketones, and acids. By and large

these are undoubtedly formed by transformation of alcohols and their nitrous esters under conditions of nitrating, and through the latter so are the other, more stable, alkyl nitrates. This conclusion rests on general chemical data about the behavior of alcohols, alkyl nitrites, and nitrates, and is wholly confirmed by direct experiments transforming a large part of residual oils into carbonyl compounds and acids through lengthy standing or heating with nitric acid in the presence of nitrogen dioxide.

Other conclusions drawn from our theory are also confirmed by experiment. Thus it follows that under nitrating conditions (when almost the only transformations of alkyls will be into compounds with NO_2 groups) the initial reaction products, practically speaking, should be nitro compound and alkyl nitrite. The probability of their formation at constant temperature, will remain constant when other factors are changed. From this one ^a may expect in experiments which satisfy the stated requirements a comparatively constant yield of the nitro compound of oxidation products, taking into consideration the hydrocarbon which entered into the reaction. This actually is the case in the nitrating of toluene at 100 degrees [Centigrade] which we have described in our third report.

NO OF TABLE AND EXPERIMENT	YIELD (IN PERCENT OF THEORETICAL)			
	$\text{C}_7\text{H}_7\text{COOH}$ (a)	RESIDUAL OIL (b)	SUM (a+b)	$\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$
Table 1, exp. 1	7.1	39.2	46.3	51.0
" 1, " 2	11.2	33.6	44.8	52.5
" 2, " 1	26.6	20.0	46.6	49.8
" 2, " 2	4.7	41.8	46.5	49.3
" 3, " 2	23.5	22.9	46.4	50.1
" 3, " 5	11.9	29.9	41.1	55.2

On that basis it may be assumed that about 55 percent of the successful collisions of benzyl with NO_2 at 100 degrees lead to the formation of phenyl-nitro-methane, and 45 percent lead to the formation of benzyl nitrite.

From data in the same report one is easily convince that the yield of the end product of oxidation -- benzoic acid -- increases in accordance with the change in experimental conditions favoring the transformation of benzyl alcohol and benzyl nitrite into that acid.

This process takes place to a large extent in the third of the above mentioned experiments whose conditions must be considered very variable in comparison with those practiced earlier, a fact which also explains the results obtained in the investigations of Konovalov, Shorygin, and other authors.

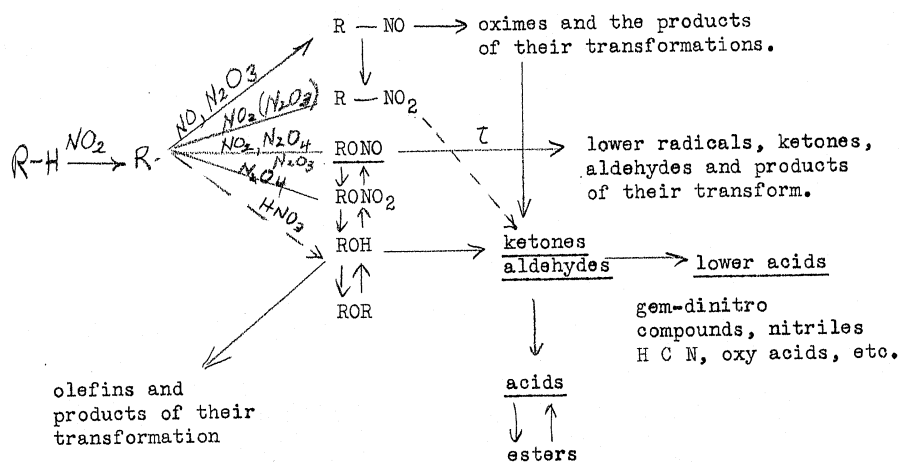
In the nitrating of cycloparaffins under the usual rigid conditions, transformation of alcohols and their nitrites should in the main lead to the formation of $\omega\omega_1$ - dicarboxylic acids. This actually does take place. Results of our detailed investigation of the action of nitrogen oxides and of nitric acid upon cyclohexane will be reported later on. The oxidation of N - paraffins $\text{C}_n \text{H}_{2n+2}$ during nitrating, if we are to take into account the observations of Konovalov about the preeminent course of the reaction into situation 2, should give chiefly acetic acid and acid $\text{C}_{n-2} \text{H}_2 (n-2)+1 \text{COOH}$, a fact confirmed by the work of Granacher (5) investigating the action of nitrogen dioxide upon undecane.

If we take into consideration all the other possible transformations of alcohols, aldehydes, ketones, and acid compounds which may arise during nitrating, then the number of products having a chance to form and be preserved under more or less variable conditions, may be very large. Of these may be mentioned lower ^{gem}-dinitro compounds, nitriles, and among the latter -- prussic acid, oxy-acids, and so forth.

Other methods of forming oxidation products, if the process is directed toward getting nitro compounds, are usually of secondary importance. We have already indicated, in our second report, the possibilities of transforming intermediate nitrous compounds - oximes - into oxidation products.

The formation of oxidation products through nitrating nitroparaffins cannot, under ordinary circumstances, have any notable significance in view of the stability of the latter toward the action of nitrogen dioxide. In this respect the role played by the transformation of primary and secondary nitro paraffins under the influence of nitric acid, is apparently also small, if we exclude the case of nitrating with a concentrated acid without the employment of a large surplus of hydrocarbon. The ease of transformations of the last kind is, of course, incomparably greater for nitro alkyl benzenes than for nitro paraffins. Some idea of the significance of this process may be formed through a comparing the yields of phenyl-nitromethane and of benzoic acid in experiments 1 and 3, table 3 of our third report.

To sum up the investigation in even greater detail, the means of forming oxidation products during the nitrating of the paraffin chain may be expressed by the following diagram:

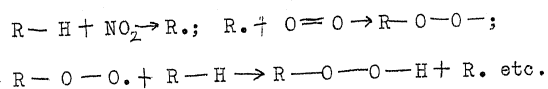


Undoubtedly, the bulk of oxidation products [illegible] transformation of alkyl nitrite $RONO$, which becomes further oxidized, by one method or another, into aldehydes, ketones, and acids, including also [illegible] -- all these compounds are underlined on the diagram. The small role played by nitro compounds in the formation of oxidation products is shown by an interrupted arrow.

The fate of alkyl nitrites during high-temperature nitrating in the

gaseous stage had been explained before (6). It is important to note that the nitrites are here the source of lower nitro compounds. Side by side with alcohols, alkyl nitrates and other esters, olefins may also be formed under these conditions to a greater or lesser degree.

Now a few words about the catalytic action of nitrogen dioxide during the oxidation of hydrogen, carbon monoxide, and paraffins. As is known, additions of insignificant quantities of nitrogen dioxide cause a sharp lowering - some 100 to 200 degrees [Centigrade] - of the ignition temperature of fulminating mixtures under low pressures. This effect is displayed at a maximum upon increasing the NO_2 concentration. After a certain concentration of NO_2 is reached, no fulmination of the mixture takes place at all and instead a slow, stationary reaction occurs (7). From our point of view these phenomena, in conformity with the established rule, are to be explained in the following way. Nitrogen dioxide, in a successful collision with hydrocarbon, forms a radical which with a very high ratio of O/NO_2 initiates a chain reaction of oxidation at R links:



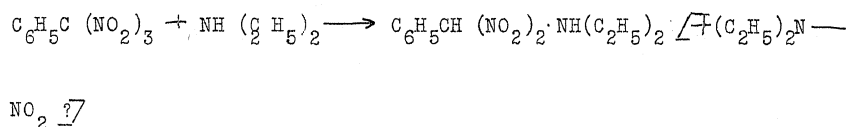
Side by side with that the molecules of NO_2 and NO on meeting the radicals break those chains, thus reducing the number of their links or not allowing their development at all. Since the effectiveness of the collisions of radicals with nitrogen oxides is greater than it is with oxygen, the increased effect of these ruptures with the increase of NO_2 concentration, leads to the observed picture. In a substantial concentration of nitrogen dioxide the reaction changes into straight nitrating. These concepts will help solve the problem of using nitrogen oxides as accelerators of atmospheric oxidation.

EXPERIMENTAL SECTION

Theoretical considerations showed that in order to insure the best yield of the sought for compounds, it was necessary to use a reactive

hydrocarbon in excess. Among the available products toluene satisfied these requirements. In order to detect benzyl nitrite, alcohol, and nitrate in the residual oil formed during the nitrating of toluene, we made use of their reaction with diethylamine. As we demonstrated in a separate report, benzyl nitrate alkylates the diethyl amine very vigorously forming benzyl-diethyl-amine, while benzyl-nitrite just as quickly nitrosates it, transforming it into nitroso-diethyl-amine. Investigation of the action of nitro-toluene and dinitro-toluene upon diethyl-amine showed no reaction.

The evidence observed upon mixing the residual oil with diethyl amine (rise in temperature, clouding, etc.) indicated an immediate reaction. Further investigation confirmed the course of the expected reactions. At the same time a side reaction with phenyl-trinitro-methane was also discovered. Traces of the latter found in the residual oil resulted in the formation of diethyl-ammonium salt of phenyl-nitro-methane. (A separate report on the formation and properties of this compound will be made). Traces of the latter found in the residual oil resulted in the formation of diethyl-ammonium salt of phenyl-nitro-methane:



Usually determination of the content of benzyl nitrate and alcohol was conducted in the following way. After a water wash the reaction mass was stirred, (as has been described (3)) with a solution of potassium bicarbonate in order to draw off benzoic acid, leaving behind the phenyl-dinitro-methane, nitrocresol, and alkali, leaving behind the phenyl nitro methane. The remainder of the reaction mass, the so-called residual oil (immediately or after separating the bulk of the hydrocarbon by vacuum distillation at a pressure of 60 millimeters and a bath temperature of about 50 degrees) was mixed with an excess of diethyl-amine and a small quantity of a 50 percent solution of potash. To complete the reaction, if the toluene began to escape, the mixture was refluxed for one (1) hour.

in a boiling water bath. In the presence of a large amount of hydrocarbon heating time was naturally prolonged, due to the sharp decrease in reaction rate in the presence of such a non-polar solvent.

After adding water we separated the solution of potash, containing nitrite, nitrate and the salt of phenyl-dinitro-methane. The presence of the former could be determined by the usual methods; isolation of phenyl-dinitro-methane took place in the way previously described (4).

For the drawing off of benzyl-diethyl-amine the residue was usually processed with a 10 percent hydrochloric acid, containing 10 percent of table salt. The acid extract was filtered with carbon and then alkalized with a strong solution of caustic potash; the remaining diethyl-amine was driven off in a water bath. The alkaline residue we separated with ether, dried with potash, and distilled, or identified in it benzyl-diethyl-amine in the form of picrate. Benzyl-diethyl-amine was identified by its boiling point and by the absence of melting point depression of picrate in a sample mixed with the product obtained from benzyl-chloride and diethyl-amine.

After drawing off the amines, the residue was processed for three hours in a shaker with a solution of sodium bisulfite. To dissolve the bisulfite compound we added warm water and evolved benzaldehyde from a separate water layer by heating with an addition of potash for half an hour at 70 degrees. The organic layer was rinsed with a sodium carbonate solution, dried with potash, and subjected to distillation under vacuum. For the isolation of benzyl alcohol we collected the fraction for toluene up to 115 degrees under 10 millimeter pressure, and washed it successively in 50 100 [cubic centimeters] of warm water. The water extract was saturated with table salt and extracted with ether.

From distillation of the extract we obtained rather pure alcohol having a boiling point of 200^o-206 degrees [centigrade]. This mixed with p-nitro-benzoyl-chloride, in the presence of alkali and a few drops of pyridine for accelerating the reaction, changed into crystalline benzyl nitrobenzoate which did not depress the melting point in a sample mixed

with a product of known structure.

For the determination of benzyl nitrite and benzyl alcohol, each separately, the following method was used. The residual oil, after amines and benzaldehyde were drawn off, was processed in the cold by a quadruple volume of concentrated hydrochloric acid and the acid extract was quickly separated. During this operation benzyl alcohol and N -nitroso-diethylamine passed into water solution as ionized compounds. Upon standing the oxonium derivative of alcohol was gradually transformed into benzyl chloride which was identified by its boiling point and by changing it into picrate of benzyl-diethyl-amine. From the acid solution by alkalization we extracted oil. Upon fractionating this under vacuum we obtained N -nitroso-diethylamine exhibiting a correct temperature at its boiling point, a corresponding odor, and giving the Liebermann reaction. A small quantity of nitroso-diethyl-amine could also be obtained from the mother liquor of picrate of benzyl-diethyl-amine, for which purpose, after the separation of alcohol, we alkalized and steam distilled it. The distillate (?) was fractionated in a vacuum at 10 millimeters of residual pressure. We collected a fraction having a boiling point of 56 - 62 degrees Centigrade which contained mainly nitroso-diethyl-amine.

When working with small quantities, or to identify small concentrations of benzyl alcohol, we would mix the residue with fuming hydrochloric or hydrobromic acids, with the addition of bisulfite for the purpose of fixing the small quantities of the free halide given off. After this stood overnight we would separate the collected acids, rinse the organic layer with water, add to the last several grams of diethyl-amine and potash and heat for 3 hours in a water bath. Then, by a method previously described, we extracted benzyl-diethyl-amine from the product of the reaction and transformed it into illegible the picrate.

Finally, to identify in the residue of the reaction product, benzyl alcohol, benzaldehyde, benzyl benzoate of dibenzyl ester, and other products of substitution in the side chain, as well as present and mixed in the illegible chain, and also nitro toluenes, we oxidized illegible it with a mixture of bichromate illegible and sulfuric acid

under experimental conditions analogous to the reaction with p-nitro toluene. After oxidizing the reaction mass, we diluted it with a triple volume of water and, maintaining this degree of dilution, steam distilled off benzoic acid and o-nitro toluene which did not enter into the reaction. The distillate ^{was made alkaline} ~~illegible~~ ^{was extracted with ether.} and o-nitro toluene ~~were driven off by 2-nitro-~~ ~~toluene ether~~. Benzoic acid was separated by acidification upon the condensation of the alkaline solution. By filtering the cooled residue in a distilling flask, in appropriate cases, we would obtain crude p-nitro benzoyl acid which we would purify first by washing with ammonia and then by crystallizing or subliming. O-Nitro toluene was identified by converting it through oxidation with permanganate into o-nitro benzoyl acid. For identifying the nitro-toluenes we reduced a fraction of the residue with stannous chloride and hydrochloric acid, then steam distilled the fraction first in acid solution and later in alkaline solution. From the obtained mixture of amines, p-toluidine was given off in the form of its acetyl derivative.

We give below results of the investigation on the composition of residual oil, produced by nitrating toluene into paraffin chain, in the most interesting cases.

1. The investigation of residual oil resulting from nitrating with nitrogen dioxide at 90-100 degrees centigrade using oxygen under conditions of experiment 2, table 1 of our third report: The yield of residual oil made up approximately 34 percent of the theoretical quantity, taking into consideration the hydrocarbon which entered into the reaction. From 33.4 grams of residual oil, after drawing off benzyl alcohol and nitroso-diethyl-amine in the form of oxonium compounds, we obtained (in grams):

Benzyl-diethyl-amine.... 2.1	Benzaldehyde..... 2.4
Nitroso-diethyl-amine.... 4.8	Residue..... 9.8
Benzyl-chloride.....14.4	

Through distillation of the residue, at 10 millimeters of pressure, were obtained the following fractions: with a boiling point at 80°-95 degrees, 3.1 grams; 95°-105 degrees, 1.9 grams; 103°-140 degrees, 1.4 grams, and 1.7 grams residue. After an analysis of samples from them by oxidation,

The following data were obtained (in grams):

	$\text{C}_6\text{H}_5\text{COOH}$	$\text{o-C}_6\text{H}_4\text{NO}_2$	$\text{p-C}_6\text{H}_4\text{NO}_2$
2.7 grams of 1st fraction	0.67	0.2	-
1.3 grams of 2nd fraction	0.18	0.2	0.14
1.3 grams of 3rd fraction	0.16	-	0.19
1.7 grams of residue	0.34	-	-

On the basis of the above demonstrated data, and the determination of the yield of o-nitro compounds (8) and of benzoic acid, the composition of the reaction product in percentages of the theoretical to the spent toluene may be expressed approximately by the following table:

Phenyl nitro methane	52.5	Benzaldehyde	2.4
Phenyl dinitro methane	2.7	Other products of substitution in the CH_3 group	2.4
Benzoic acid	11.2		
Benzyl nitrate	1.88	o-Nitro toluene	1.2
Benzyl nitrite	6.4		
Benzyl alcohol	7.1	p-Nitro toluene	1

Not taken into account, 10

Undoubtedly the figures given for benzyl alcohol are larger, and those given for benzyl nitrate are significantly lower, than the actual ones for the latter. This is due to the nature of the hydrolyzing process in alkaline solution. This accounts partly for the loss of weight noted. Analyzing residual oil obtained from nitrating with nitrogen dioxide without using oxygen (experiment of type No. 1, table report III), gave complex results.

2. Investigation of the composition of 15.0 grams of residual oil from the nitrating with nitric acid ~~illegible~~ ^{of sp. gravity} 1.5 under conditions of experiment 3, table 3, report III, gave the following products: 2.1 grams benzaldehyde, 1.4 grams benzyl diethyl amine, 3.9 grams benzyl alcohol, 5.3 grams residue by whose oxidation was obtained 2.4 grams of benzoic acid, 0.9 grams of o-nitro toluene, and 0.6 grams of p-nitro benzoic acid. An analysis of the residual oil of an analogous experiment with the employment

of oxygen gave similar results.

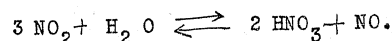
3. In experiments investigating the reaction of nitrogen dioxide with toluene at usual temperatures, the following preliminary data were obtained. In the case of the reaction of nitrogen dioxide having a concentration of 1-3 percent in toluene, using oxygen to remove nitrogen oxide, the main products of the reaction were benzyl alcohol and its esters and some nitrates. Thus, in one of the experiments described in the second report (experiment No. 3 of the last table), the residual oil contained at least 30 percent of benzyl nitrate.

Total data on the composition of the reaction product from 40 grams N_2O_4 in 2# l. toluene after four days of standing, at 25 degrees in the presence of 30 grams $Ca(NO_3)_2$ and with constant saturation by oxygen, may be expressed approximately by the following table:

	Grams	Percent
Phenyl-nitro-methane	7.7	11.2
Benzyl alcohol and its esters	29.6	43.2
Benzaldehyde	7.5	14.2
Benzoic acid	2.7	4.4
o- and p- Nitro toluenes	9.4	13.6
Nitro cresols	2.2	2.2
Residual products	7.7	11.2

The correlation of p- and p- nitro toluenes is close to 1:1.

The increased yield of nitro derivatives is partly explained by the significant concentration of nitric acid, formed in this case through a shifting of the equilibrium:



from left to right, due to the removal of nitrogen oxide by oxygen.

In experiments of large dilution, but without the employment of oxygen or with saturation by nitrogen oxide (No 2 and 3 of the last table of the second report), in conformity with theory, the reaction proceeded slowly and the main product was phenyl-dinitro-methane. This yield reached almost 50 percent of theoretical. The yield of residual oil indicated that

about 35 percent of the toluene entered into the reaction. The oil consisted basically of benzyl alcohol and its ethers and contained very little

o-nitro toluenes. In the case of taking a small residue from the toluene (i.e. with a small possibility of dissociation of N_2O_4) in conformity with theory the reaction proceeded very slowly and, as a result of the high "strength" of nitric acid and of the excess of N_2O_4 , led to the formation of a large quantity of nitro-toluenes and benzoic acid. Thus, for instance, after 50 milliliters of toluene, 40 grams of nitrogen dioxide, and 15 grams of anhydrous blue vitriol were left standing for a month in an average temperature of 20 degrees Centigrade the following data about the composition of the reaction product was found:

	Grams	Percent
Phenyl-nitro-methane	2.1	7.2
Phenyl-dinitro-methane	2.6	9.0
Phenyl-trinitro-methane	1.8	6.2
Benzoic acid	4.5	15.5
Benzyl alcohol and its esters	3.0	10.3
Nitro toluenes	10.5	36.2
Other products	4.5	15.5

In further investigations undertaken the formation of benzyl nitrate and alcohol was observed from the nitrating of toluene with nitrogen dioxide in sealed tubes at both usual and elevated temperatures, and also in Konovalov's method, using diluted nitric acid. We have also shown the formation of alcohols and their esters in the nitrating of m- xylene, diphenyl methane and ethyl benzene, cyclohexane, n- pentane, and other hydrocarbons. We shall report on these in detail later on.

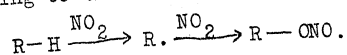
ON THE STABILITY OF BENZYL NITRATE AND NITRITE

Benzyl nitrate is stable during storing. Heating it in toluene, in a boiling water bath, does not bring about any noticeable disintegration. Benzyl nitrite on the other hand, was almost entirely disintegrated after being on hand for a month. Decomposition products consisted mainly of benzaldehyde (about 60 percent), benzoic acid, and tar. In heating, in a

water bath, 25 grams of freshly prepared benzyl nitrite (boiling point 56 degrees at 10 millimeters mixed with 50 milliliters of carbon tetrachloride, a significant isolation of nitrogen oxide took place. The distillation of the remainder, at 10 millimeters of residual pressure, gave the following fractions: I from 50-60 degrees, 12.3 grams; II from 90-120 degrees, 2.5 grams; III from 120-140 degrees, 2.5 grams, and about 5 grams of tar residue. The first fraction consisted mainly of the non-decomposed benzyl nitrite and benzaldehyde. Composition of the high-boiling fractions was not studied more closely; undoubtedly, they contained a significant quantity of benzyl benzoate and of dibenzyl ether. The investigation of these fractions may shed light on the composition and derivation of the corresponding parts of residual oil.

CONCLUSIONS

1. The basic, primary product of oxidation, in the reaction of nitrogen oxides and nitric acid upon the paraffin chain, is alkyl nitrite which is formed according to the scheme:



The production of alcohols and their esters may also come about in the reaction of radicals with N_2O_4 , N_2O_3 , $HONO_2$, and through a reaction with oxygen.

2. In the liquid phase of nitrating there arises an equilibrium between alcohol, its ether, and the nitrous, nitric, and other possible esters.

3. Further products from oxidation and decomposition arise chiefly from transformation, under the conditions of reaction, of alcohols, alkyl nitrates, to a lesser degree nitro compounds, and to a very insignificant degree, nitro derivatives.

4. Peculiarities of the action of nitrogen dioxide upon the oxidation of paraffins by oxygen can be explained by comparing, on one hand, its action in exciting the formation of radicals and reactive chains and, on the other, the ability of NO_2 and NO in stopping production of reactive chains.

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